



ORIGINAL ARTICLE

Production & Characterization of Activated Carbon Membranes

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The objective of this work was the production and characterization of ultrafiltration membranes composed of micropores activated carbon (AC) saturated with a solvent, in epoxy resin matrix. In order to produce these composite membranes with a desired final porosity of 60%, national grade micropores powder AC with different particle size distribution was used. The AC and the composite activated carbon membranes (CACMs) were characterized for their thermal stability, chemical composition, specific surface area, and porosity. The results indicate that AC has a high specific surface area; the apparent porosity of the CACMs is in the range of 50%-58% with thermal stability up to 370°C, in which the decomposition of the organic constituents started. Composition and structure of the CACMs were found to be almost of the epoxy resin and AC with the absence of the solvent. It can be concluded that the CACMs developed in this work can be satisfactorily used in applications of ultrafiltration.

KEY WORDS: Activated carbon; Epoxy resin; Composite membranes; Ultrafiltration.

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1. Introduction

Activated carbon (AC) is recognized as effective and reliable means in removing impurities. It has a tremendous adsorptive capacity, an affinity for a wide variety of dissolved organics and chlorine^[1] that is why it has been employed in a wide range of applications on an industrial scale including technologies for the purification of gases, the removal of organic pollutants from water (i.e., purification of drinking water and wastewater), and also medical applications. The primary raw material used to produce AC is any organic ma-

terial with high carbon content (coal, wood, peat, coconut shells etc.). The carbon-based material is converted to AC by thermal decomposition in a furnace using a controlled atmosphere and heat or by other physical and chemical methods. The resultant product has an incredibly large surface area per unit volume, and a network of submicroscopic pores where adsorption takes place. The walls of the pores provide the surface layer molecules essential for adsorption^[2]. In simple terms, physical adsorption occurs because all molecules exert attractive forces, especially molecules at the surface of a solid, and these surface molecules seek other molecules to adhere to: the large internal surface area of carbon has many attractive forces that work to attract other molecules.

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Membrane filtration is expected to be one of the alternatives for complicated, laborious, and costly processes used for purification, because in principle it can make the process very compact and the treatment cost lower. However, membranes to be employed in water treatments must satisfy the following requirements: the practical water flux through the membrane is essential; suspended solids and dissolved organics should be simultaneously removed; fouling of the membrane should be minimized; and sufficient mechanical strength is needed. Unfortunately, it is difficult so far to find a commercial membrane which meets all the above-mentioned demands. Composite AC membranes (CACM's) are considered to be a promising candidate for this purpose^[3].

Epoxy resin (to be used as a matrix for the CACM's) is widely used in industrial applications in relation to adhesives, coatings, electronics, and aerospace structures. Due to its attractive mechanical and chemical properties, such as excellent bonding ability, high tensile and compressive strengths, good chemical resistance, and high heat distortion temperature, epoxy is the dominant matrix material for lightweight polymer-matrix structural composites, such as carbon fiber composites. The superior mechanical and chemical properties of epoxy are due to the three-dimensional network structure that results from the curing process, in which a low molecular weight resin is transformed into a high molecular weight polymer^[4-6]. However, the mechanical properties of this polymer matrix, such as the strength, modulus, and toughness of the epoxy resins, may not be sufficient for some end-use applications. It is therefore desirable to modify the polymer matrix to achieve such purposes. The addition of fillers to polymer matrix is a fast and cheap method to modify the properties of the base materials^[7].

Wang *et al.*^[8] used natural sponge as a template to produce carbon/epoxy resin composites with interpenetrating network structure. Carbon with a network structure in the composites was shown to stabilize the coefficient of friction of epoxy resin. The carbon also reduces the wear rate of the epoxy resin remarkably^[8]. The effect of multi-walled carbon nanotube (MWCNT) addition on mechanical properties of epoxy resin was investigated by Vijay Kumar Srivastava to obtain tensile strength, compressive strength, and Young's modulus from load *versus* displacement graphs. The result shows that tensile strength, compressive strength, and Young's modulus of epoxy resin were increased with the addition of MWCNT fillers^[9].

In this work, the objective was the production and characterization of AC and epoxy resin composite membranes for ultrafiltration applications, specifically speaking this study is part of a project intended to construct innovated prototype of tubular, multichannel membranes similar to the capillary polymeric membranes, for potential use in hemodialysis, purification of drink water, and desalination of water in the Northeast of Brazil. All applications look forward to overcome the high cost of the imported polymeric membranes for hemodialysis and solving the lack of pure drinking water in that region.

2. Materials and Methods

To obtain ultrafiltration membranes, micropores AC powder was used with the following particle size distributions:

as received (AR), less than sieve #170 and #325. The AC is national grade produced by Carbomafra from coconut shell. The CACMs were produced with volume fractions of AC impregnated with a solvent (ethyl acetate) to saturate the pores and epoxy resin: the volumetric fraction of the pores that is needed for an adequate permeability is projected to be 60%. The mixture of the constituents having the required volumetric fractions (40% resin and 60% AC) was made in tubular shapes; after curing at 40 °C the material was fired at 150 °C for the complete evaporation of the solvent and then it was ready for analysis.

To characterize the AC and the CACMs the following techniques were used: specific surface area based on the adsorption and desorption isotherms was determined by nitrogen adsorption at 77 K system (NOVA-1200 gas sorption analyzer of Quanta chrome Corporation), and each sample was degassed at 150 °C prior to the adsorption test. The collected data was analyzed by NovaWin-9.0 program employing the Dubunin-Radushkevich (DR) equation, which gives evaluation of the total surface area and total pore volume and allows the calculation of the average pore radius for relatively hard materials or materials with high surface area like AC. The apparent porosity, specific mass, and specific mass of the solid part were measured by Arquimedes method for at least three samples of the membranes and the average was calculated. To evaluate the thermal stability of the CACMs about 20 mg from each of the samples was subjected to thermogravimetric analysis (TGA) runs carried out in flowing nitrogen gas with heating rate of 20 °C/min using Netzsch STA 409 equipment. To verify the structure of the CACMs and to insure the full evaporation of the solvent from the pores, Fourier Transform Infrared (FTIR) spectra of fresh powder samples of CACMs were obtained by making a pellet mixing 100 mg of KBr with 1 mg of membrane sample and measuring in the range of 400 cm⁻¹ to 4,000 cm⁻¹ using Nicolet-4700 FTIR spectrometer of Thermo Scientific.

3. Results and Discussion

3.1 Specific Surface Area, Pore Volume and Pore Width Analysis

The adsorptive capacity of adsorbent is related to its internal surface area and pore volume. Generally, the larger the specific surface area of the adsorbent, the better its adsorptive performance will be^[10]. Adsorption and desorption isotherms were evaluated by DR routine and the results are listed in Table 1, which shows the high value of the specific surface area of the AR AC as well as the fine AC of sieves

Table 1 Specific surface area and average pore size of activated carbon as obtained from isotherms by DR equation

Sample	Micropore surface area (m ² /g)	Micropore volume (cc/g)	Average pore width (nm)
AR-micro	716.744	0.253	5.03
AC #170	769.407	0.272	5.33
AC #325	818.100	0.289	5.09

AR: as received; AC: activated carbon.

Table 2 The apparent specific mass, apparent specific mass of the solid part, and apparent porosity of the CACMs obtained by Arquemedes principle

Sample	Apparent specific mass (g/cm ³)	Apparent specific mass of the solid part (g/cm ³)	Apparent porosity (%)
CC#AR	0.580	1.386	58.22
CC#170	0.588	1.350	56.64
CC#325	0.609	1.324	53.00

#170 and #325. However, these values were higher than 534 m²/g and 657 m²/g reported for carbon black samples prepared from coconut husk and jute fibers^[11].

It can be noted that the finest are the AC particles (AC#325), the more they account for a relatively largest specific surface area and micropore volume, and this result is in agreement with the findings of Zhang *et al.*^[12]. Beside specific surface area and pore volume, pore diameter (or pore width) is also an important characteristic of the AC; the average pore size was found to be in order of 5 nm varied slightly within the limit of sensitivity of the equipment, this value classified this AC as mesopores. The volume of micro- and mesopores can be an important parameter depending on the type of pollutant to be removed as well as the media from which they have to be removed. Thus, preparation conditions of the AC to obtain an optimal micro- or mesopores is very important^[13].

The results of apparent porosity, specific mass, and the specific mass of the solid part of the AC are shown in Table 2.

Taking into account that the apparent porosity of the CACMs was designed to be of 60%, however, in practice, it was found to be 56% in average: this apparent porosity is reasonable for liquid permeation but it can be improved. It was also noted that the apparent porosity decreases with the sieve size: the finest the AC, the lower the apparent porosity. The density of the CACMs did not vary much with the sieve size.

3.2 Thermogravimetric Analysis (TGA)

TGA curve with its derivative (DTG) of the AR AC is shown in Fig. 1. It can be seen that there is a small amount of weight losses below 100 °C (T_1) due to desorption of the physisorption water. For the carbon materials, to some extent, the amounts of physisorption water reflect their hydrophilicity and pore structures. The AC exhibits the largest water adsorption capacity in ambient condition, implying its superior hydrophilicity and pore volume^[14,15].

In Fig. 2, of the as received CACM (CC-AR), two stages of weight loss are shown by the DTG curves: the first one below 100 °C (T_1) is attributable to the removal of mainly hygroscopic water. On the other hand, the second one is the pronounced weight loss that took place in the range of 360 °C–380 °C which can be ascribed to the pyrolysis of epoxy resin.

In Table 3, the TGA results of the AC and CACMs were summarized.

The humidity loss temperatures (T_1) are a little bit higher in the CACMs than in the AR AC. The decomposition

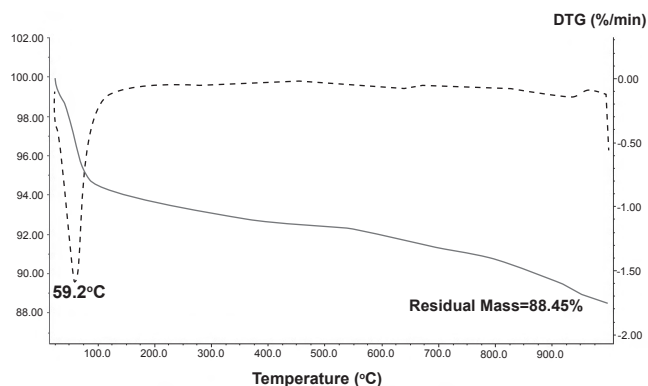


Fig. 1 The TGA curve and its derivative showing the thermal decomposition temperature and the residual mass of AR AC.

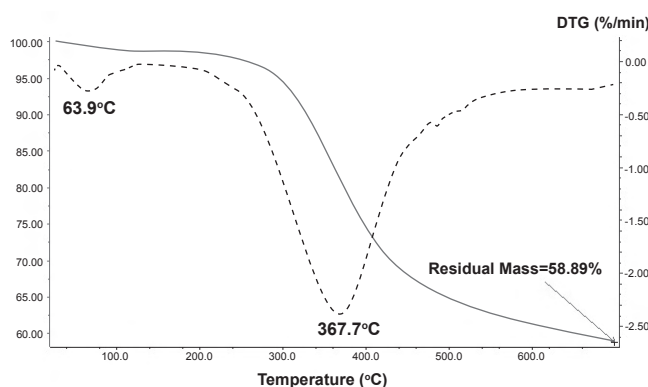


Fig. 2 The TGA curve and its derivative of CACM (CC-AR) showing the thermal decomposition temperatures and the residual mass of its constituents.

Table 3 Decomposition temperature and residual mass of the as received activated carbon and the CACMs

Sample	T_1 / °C	T_2 / °C	Residual mass (%)
AR	59.2	—	88.45
CC#AR	63.9	367.7	58.89
CC#170	76.6	375.4	33.99
CC#325	76.2	372.5	52.82

temperature (T_2) of the epoxy starts at 368 °C in inert gas atmosphere; this will be different in an oxidative one.

Studies on CACMs and epoxy resin showed that the introduction of AC decreases the curing temperature of the epoxy resin: this effect is consistent with the high specific surface area of AC^[16–18], that is to say: increasing the specific surface area of AC accelerates the curing of epoxy resin. In this study, TGA did not show the curing temperature of epoxy resin because the curing occurred during the preparation step of the CACMs. The residual mass of 88.45% was found after heating AC up to 1,200 °C. This confirms the high stability of the AC in contrast to the lower stability of the CACMs, and this is obvious due to pyrolysis of the epoxy resin upon heating.

3.3 Fourier Transform Infra-Red (FTIR)

Fig. 3 compares the FTIR spectra of the CACMs, epoxy resin, and the solvent used to impregnate the AC.

It can be inferred that the structure of the CACMs is practically of epoxy resin characteristic bands with intensities consistent with the proportions adopted during the preparation of the composites, and it is very clear that there is no trace left of the solvent in the CACMs which assure its complete evaporation.

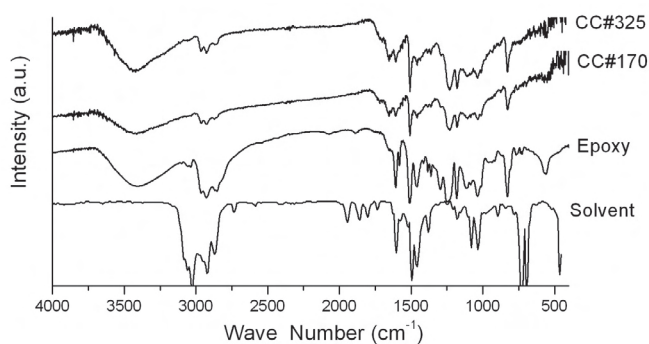


Fig. 3 FTIR spectra of the CACMs compared with the epoxy resin and the solvent spectra.

4. Conclusions

The characterization showed the following satisfactory results:

- Concerning the specific surface area and apparent porosity, they are reasonable considering that the volumetric fraction of the pores which is needed for adequate permeability is between 40%-75%;
- thermal stability, another important factor in the applications of ultra filtration membranes, was achieved in the CACMs developed in this work;
- the sieve size is shown to have an effect on the apparent porosity but it has no significant effect on either TGA or FTIR results;
- the complete removal of the solvent (after helping in mixing the AC and the resin) from the CACMs has no effect on their structural integrity.

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